Enantioselective Organocatalytic α-Fluorination of Aldehydes

Teresa D. Beeson and David W. C. MacMillan*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Supporting Information

General Information. Commercial reagents were distilled prior to use following the guidelines of Perrin and Armarego.[1] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using forced-flow chromatography on EMD Silica Gel 60 230-400 mesh or Davisil® Silica Gel 200-425 mesh according to the method of Still.[2] Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by fluorescence quenching using potassium permanganate stain. High Performance liquid chromatography (HPLC) and Gas liquid chromatography (GLC) assays to determine enantiometric excess were developed using racemic samples.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Varian Mercury 300 (300 MHz, 75 MHz and 282 MHz respectively) as noted, and are internally referenced to residual protio solvent signals. Data for ^{1}H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C and ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant (Hz). IR spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the California Institute of Technology Mass Spectral facility. Gas liquid chromatography (GLC) was performed on a Hewlett-Packard 6850 Series gas chromatograph equipped with a split-mode capillary injection system and flame ionization detectors using a Macherey-Nagel Hydrodex-B-TBDAc (50 m x 0.25 mm) column. High Performance liquid chromatography (HPLC) was

performed on a Hewlett Packard 1100 Series chromatograph using a Chiralcel® OJ column (25 cm, 5 cm guard) as noted.

General Procedure for the α-Fluorination of Aldehydes: To a 25 mL round-bottom flask equipped with a magnetic stir bar and charged with **1** (*R*)-5-benzyl-2,2,3,-trimethylimidazolidin-4-one dichloroacetic acid salt (139 mg, 0.400 mmol) and *N*-fluorobenzenesulfonimide (3.15 g, 10.0 mmol) was added THF (9.0 mL) and *i*PrOH (1.0 mL). The mixture was stirred at rt until homogeneous then cooled to –10°C. The aldehyde substrate (2.0 mmol) was added and the reaction mixture stirred 12 h. The reaction was cooled to -78 ºC, diluted with 10 mL Et_2O and filtered through a pad of Davisil® Silica Gel, eluting with Et_2O. Me_2S (5.0 mL) was added forming a white precipitate. The resulting mixture was washed with Sat. $NaHCO_3$ (3 x 150 mL) and brine (1 x 150 mL) and dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting oil was dissolved in CH_2Cl_2 (12 mL) and EtOH (8 mL) and $NaBH_4$ (189 mg, 5.0 mmol) was added. After 30 min. the reaction was cooled to 0°C and Sat. NH_4Cl (150 mL) was added. The mixture was warmed to rt and stirred vigorously 1 h. The cloudy suspension was allowed to separate and 75 mL of CH_2Cl_2 was added. The solution was extracted with CH_2Cl_2 (3 x 100 mL) and the combined organics washed with Sat. $NaHCO_3$ (3 x 150 mL) and brine (1 x 150 mL) and dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification of the resulting oil by forced flow chromatography afforded the title compounds. The enantioselectivity was determined either by chiral GLC analysis, or chiral HPLC analysis after acylation of the alcohol with 2-naphthoylchloride.

Starting Materials

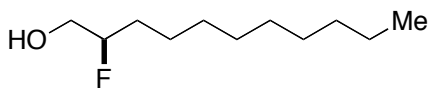
Ethyl 5-formylpentanoate: To a flask containing ethyl 6-hydroxyhexanoate (4.07 mL, 25.0 mmol) in CH_2Cl_2 (25 mL) was added TEMPO (391 mg, 2.50 mmol) followed by iodobenzene diacetate (8.86 g, 27.5 mmol). The reaction was stirred 2 hours and then diluted with CH_2Cl_2 (100 mL). Saturated aqueous solution of $Na_2S_2O_3$ (100 mL) was added and extracted with CH_2Cl_2 (3 x 50 mL). The combined organics were washed with saturated aqueous $NaHCO_3$ (150 mL) and brine (150 mL), dried over Na_2SO_4, and

concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography (20-40% Et_2O/pentanes) to provide the title compound, which was identical to the reported literature compound.[3]

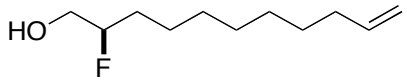
***tert*-Butyl 4-(formylmethyl)piperidine-1-carboxylate:** To a flask containing *tert*-butyl 4-(2-hydroxyethyl)piperidine-1-carboxylate (4.4 g, 19.2 mmol) in CH_2Cl_2 (20 mL) was added TEMPO (300 mg, 1.92 mmol) followed by iodobenzene diacetate (6.8 g, 21.1 mmol). The reaction was stirred 3 hours and then diluted with CH_2Cl_2 (100 mL). Saturated aqueous solution of $Na_2S_2O_3$ (100 mL) was added and extracted with CH_2Cl_2 (3 x 50 mL). The combined organics were washed with saturated aqueous $NaHCO_3$ (150 mL) and brine (150 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography (40-70% Et_2O/pentanes) to provide the title compound, which was identical to the reported literature compound.[4] ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 154.7, 79.4, 50.3, 43.7, 31.9, 30.6, 28.4.

Adamantylacetaldehyde: To a flask containing 2-adamantyl-1-ethanol (5 g, 27.7 mmol) in CH_2Cl_2 (28 mL) was added TEMPO (433 mg, 2.77 mmol) followed by iodobenzene diacetate (9.8 g, 30.5 mmol). The reaction was stirred 1 hour and then diluted with CH_2Cl_2 (100 mL). Saturated aqueous solution of $Na_2S_2O_3$ (100 mL) was added and extracted with CH_2Cl_2 (3 × 50 mL). The combined organics were washed with saturated aqueous $NaHCO_3$ (150 mL) and brine (150 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography (5% Et_2O/pentanes) to provide the title compound, which was identical to the reported literature compound.[5]

α-Fluoro Alcohols

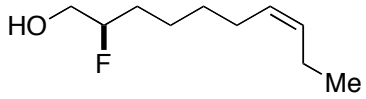


(*R*)-2-Fluoro-1-undecanol (Table 2, entry 1): Prepared according to the general procedure from undecanal (411 μL, 2.00 mmol) to afford a colorless oil. Purification on silica gel (10-50% Et_2O/Pentanes) afforded (*R*)-2-fluoro-1-undecanol as a colorless solid (261 mg, 70% yield, 94% ee). IR (film) 3271 3171, 2954, 2914, 2848, 1470, 1071, 842.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$). δ 4.56 (dm, *J* = 46.8 Hz, 1H, FC**H**), δ 3.59-3.77 (m, 2H, OC$\mathbf{H_2}$), δ 1.89 (s, 1H, -O**H**), 1.20-1.78 (m, 16H, (C$\mathbf{H_2}$)$_\mathbf{8}$), δ 0.88 (t, *J* = 6.9 Hz, 3H, C$\mathbf{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ; 96.3 (d, *J* = 166.3 Hz), 65.1 (d, *J* = 21.3 Hz), 31.9, 30.9 (d, *J* = 20.3 Hz), 29.5, 29.4 (d, *J* = 3 Hz), 29.3, 24.9, 24.9, 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –189.6 (m). HRMS (EI+) exact mass calculated for $[M-H]^+$ ($C_{11}H_{22}FO$) requires *m/z* 189.1655, found *m/z* 189.1660. $[\alpha]_D$ = 7.6 (c = 1.0, $CHCl_3$).[6] Enantiopurity was determined by chiral HPLC analysis of the 2-naphthoyl derivative (Chiralcel®OJ Isocratic 3% *i*-PrOH/Hexanes). t_R(major) = 11.4 min. t_R(minor) = 15.0 min.

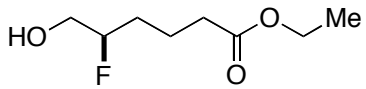


(*R*)-2-Fluoroundec-10-en-1-ol (Table 2, entry 2): Prepared according to the general procedure from undec-10-enal (416 μL, 2.00 mmol) to afford a colorless oil. Purification on Davisil® silica gel (10-20% EtOAc/Pentanes) afforded (*R*)-2-fluoroundec-10-en-1-ol as a colorless solid (296 mg, 79% yield, 94% ee). IR (film) 3214, 2918, 2848, 1641, 1460, 1348, 1073, 990.7, 914.2, 837.8, 806.0, 757.8, 724.4, 668.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$). δ 5.74-5.87 (m, 1H, $CH_2C\mathbf{H}=CH_2$), δ 4.90-5.03 (m, 2H, $CH_2CH=C\mathbf{H_2}$), δ 4.57 (dm, 1H, *J* = 50.7 Hz, FC**H**); δ 3.60-3.80 (m, 2H, OC$\mathbf{H_2}$), δ 2.03 (q, 2H, *J* = 14.1, and 7.5 Hz, C$\mathbf{H_2}$CH=CH_2), δ 1.83 (t, 1H, *J* = 6.6 Hz, -O**H**), δ 1.26-1.76 (m, 12H, FCH(C$\mathbf{H_2}$)$_\mathbf{6}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ; 139.1, 114.2, 94.8 (d, *J* = 166.5 Hz), 65.1 (d, *J* = 21.8 Hz), 31.7, 30.9 (d, *J* = 20.0 Hz), 29.3, 29.3, 29.0, 28.8, 24.9 (d, *J* =

3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ: –189.6 (m). HRMS (EI+) exact mass calculated for $[M+\bullet]^+$ ($C_{11}H_{21}FO$) requires *m/z* 188.1576, found *m/z* 188.1575. $[\alpha]_D$ = 8.1 (c = 1.0, $CHCl_3$). Enantiopurity was determined by chiral HPLC analysis of the 2-naphthoyl derivative (Chiralcel®OJ Isocratic 3% *i*-PrOH/Hexanes). t_R(major) = 15.7 min. t_R(minor) = 22.7 min.

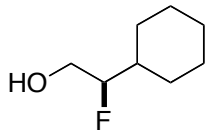


(*R*)-(*Z*)-2-Fluorodec-7-en-1-ol (Table 2, entry 3): Prepared according to the general procedure from (*Z*)-dec-7-enal (366 μL, 2.00 mmol) to afford a yellow oil. Purification on silica gel (5-20% EtOAc/Pentanes) afforded (*R*)-(*Z*)-2-fluorodec-7-en-1-ol as a pale yellow liquid (283 mg, 81% yield, 94% ee). IR (film) 3369, 3006, 2935, 2861, 1462, 1376, 1172, 1056, 843.1 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.26-5.42 (m, 2H, $CH_2C\mathbf{H}=\mathbf{H}CCH_2$), δ 4.56 (dm, 1H, *J* = 50.5 Hz, FC**H**), δ 3.62-3.76 (m, 2H, O$C\mathbf{H_2}$), δ 1.98-2.10 (m, 4H, $C\mathbf{H_2}CH=HCC\mathbf{H_2}$), δ 1.89 (t, 1H, *J* = 6.4 Hz, -O**H**), δ 1.32– 1.74 (m, 6H, $CFH(C\mathbf{H_2})_3$), δ 0.95 (t, 3H, *J* = 7.4 Hz, $C\mathbf{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 132.0, 128.7, 94.7 (d, *J* = 166.5 Hz), 65.1 (d, *J* = 21.3 Hz), 30.9 (d, *J* = 20.0 Hz), 29.5, 26.8, 24.5 (d, *J* = 5.0 Hz), 20.5, 14.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –189.6 (m). HRMS (EI+) exact mass calculated for $[M+\bullet]^+$ ($C_{10}H_{19}FO$) requires *m/z* 174.1420, found *m/z* 174.1421. $[\alpha]_D$ = 5.6 (c = 1.0, $CHCl_3$). Enantiopurity was determined by chiral HPLC analysis of the 2-naphthoyl derivative (Chiralcel®OJ Isocratic 0.5% *i*-PrOH/Hexanes). t_R(major) = 32.2 min. t_R(minor) = 51.9 min.

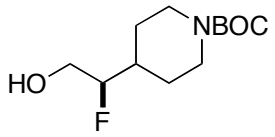


(*R*)-Ethyl 5-fluoro-6-hydroxyhexanoate (Table 2, entry 4): Prepared according to the general procedure from ethyl 5-formylpentanoate (319 μL, 2.00 mmol) to afford a colorless oil. Purification on silica gel (20-40% EtOAc/Pentanes) afforded (*R*)-ethyl 5-fluoro-6-hydroxyhexanoate as a colorless liquid (274 mg, 77% yield, 91% ee). IR (film)

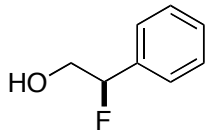
3436, 2942, 1733, 1453, 1376, 1165, 1096, 1065, 1035, 849.9, 772.2 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.57 (dm, 1H, *J* = 49.4, FC**H**), δ 4.12 (q, 2H, *J* = 7.2 Hz, $CO_2C\mathbf{H_2}$), δ 3.60-3.78 (m, 2H, $OC\mathbf{H_2}$), δ 2.34 (t, 2H, *J* = 7.0 Hz, $C\mathbf{H_2}CO_2$), δ 2.04 (s, 1H, -O**H**), δ 1.50-1.88 (m, 4H, $CFH(C\mathbf{H_2})_2$), δ 1.24 (t, 3H, *J* = 7.2 Hz, $C\mathbf{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.3, 94.2 (d, *J* = 167.3 Hz), 64.8 (d, *J* = 21.7 Hz), 60.4, 33.8, 30.2 (d, *J* = 20.6 Hz), 20.4 (d, *J* = 5.0 Hz), 14.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ: –190.3 (m). HRMS (EI+) exact mass calculated for $[M+H]^+$ ($C_8H_{16}FO_3$) requires *m/z* 179.1084, found *m/z* 179.1083. $[\alpha]_D$ = 5.1 (c = 1.0, $CHCl_3$). Enantiopurity was determined by chiral HPLC analysis of the 2-naphthoyl derivative (Chiralcel®OJ Isocratic 10% EtOH/Hexanes). t_R(major) = 47.7 min. t_R(minor) = 68.7 min.



(*R*)-2-Cyclohexyl-2-fluoro-1-ethanol (Table 2, entry 5): Prepared according to the general procedure from 2-cyclohexyl-1-ethanol (291 μL, 2.00 mmol) to afford a colorless oil. Purification on silica gel (10-50% Et_2O/Pentanes) afforded (*R*)-2-cyclohexyl-2-fluoro-1-ethanol as a colorless liquid (282 mg, 96% yield, 99% ee). IR (film) 3369, 2928, 2854, 1450, 1091, 1074, 1058, 1024, 977.7, 891.8, 858.9, 837.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.28 (dm, 1H, *J* = 49.2 Hz, FC**H**), δ 3.68-3.81 (m, 2H, $OC\mathbf{H_2}$), δ 1.83–1.94 (m, 2H, $C\mathbf{H_2}$), δ 1.56–1.84 (m, 5H, $(C\mathbf{H_2})_2$ and O**H**), δ 0.99–1.34 (m, 5H, $(C\mathbf{H_2})_2$ and CFHC**H**); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 98.4 (d, *J* = 168.3 Hz), 63.2 (d, *J* = 26.2 Hz), 30.2 (d, *J* = 19.1 Hz), 28.1 (dd, *J* = 22.7, 6.0 Hz), 26.1, 25.7 (d, *J* = 12.6 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ: –194.7 (m). HRMS (EI+) exact mass calculated for $[M+\bullet]^+$ ($C_8H_{15}FO$) requires *m/z* 146.1107, found *m/z* 146.1101. $[\alpha]_D$ = -0.26 (c = 1.0, EtOH). Enantiopurity was determined by GLC using a Macherey-Nagel Hydrodex-B-TBDAc (50 m x 0.25 mm) column (100 °C isotherm); (*R*) isomer t_r = 79.9 min and (*S*) isomer t_r = 88.8 min.

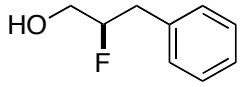


(*R*)-*tert*-Butyl 4-(1-fluoro-2-hydroxyethyl)piperidine-1-carboxylate (Table 2, entry 6): Prepared according to the general procedure from *tert*-butyl 4-(formylmethyl)piperidine-1-carboxylate (455 mg, 2.00 mmol) to afford a colorless oil. Purification on silica gel (25-50% EtOAc/Pentanes) afforded (*R*)-*tert*-Butyl 4-(1-fluoro-2-hydroxyethyl)piperidine-1-carboxylate as a colorless oil (422 mg, 85% yield, 98% ee). IR (film) 3430, 2930, 1692, 1671, 1427, 1365, 1283, 1241, 1170, 1084, 1040, 971.6, 940.0, 857.2, 770.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.06-4.40 (m, 3H, $N(C\mathbf{H_a}CH_b)_2$, and $FC\mathbf{H}$), δ 3.69-3.83 (m, 2H, $OC\mathbf{H_2}$), δ 2.68 (br m, 2H, $N(CH_aC\mathbf{H_b})_2$), δ 2.01 (t, 1H, J = 6.0 Hz, -O**H**), δ 1.80–1.87 (m, 2H, $(C\mathbf{H_a}CH_bCH_2)_2N$), δ 1.51–1.67 (m, 1H, CHFC**H**), δ 1.44 (s, 9H, $(C\mathbf{H_3})_3$), δ 1.22-1.32 (m, 2H, $(CH_aC\mathbf{H_b}CH_2)_2N$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.7, 97.3 (d, J = 170.0 Hz), 79.5, 62.8 (d, J = 22.0 Hz), 60.4, 37.1 (d, J = 19.7 Hz), 28.4, 27.3, 27.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ: –194.5 (bs). HRMS (EI+) exact mass calculated for $[M+\bullet]^+$ ($C_{12}H_{22}FNO_3$) requires m/z 247.1584, found m/z 247.1587. $[\alpha]_D$ = 3.0 (c = 1.0, $CHCl_3$). Enantiopurity was determined by chiral HPLC analysis of the 2-naphthoyl derivative (Chiralcel®OJ Isocratic 10% EtOH/Hexanes). t_R(major) = 28.3 min. t_R(minor) = 41.1 min.

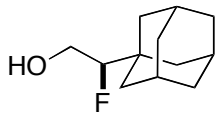


(*R*)-2-Fluoro-2-phenyl-1-ethanol (Table 2, entry 7): Prepared according to the general procedure from phenylacetaldehyde (234 μL, 2.00 mmol) to afford a colorless oil. Purification on silica gel (10-50% Et_2O/Pentanes) afforded (*R*)-2-fluoro-2-phenyl-1-ethanol as a colorless liquid (152 mg, 54% yield, 99% ee), which matched literature data.[7] IR (film) 3369, 1496, 1454, 1078, 1043, 877.9, 834.2, 757.3, 698.8 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32-7.41 (m, 5H, $C_6\mathbf{H_5}$), δ 5.57 (ddd, 1H, J = 48.9, 7.7, and 5.2 Hz, $FC\mathbf{H}$), δ 3.73-4.01 (m, 2H, $OC\mathbf{H_2}$), δ 2.18 (dd, 1H, -O**H**); ^{13}C NMR (75 MHz, $CDCl_3$)

δ: 136.3 (d, *J* = 19.6 Hz), 128.8 (d, *J* = 2.0 Hz), 128.6, 125.7 (d, *J* = 6.9 Hz), 94.8 (d, *J* = 170.9 Hz), 66.6 (d, *J* = 24.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –187.0 (ddd, *J* = 12.8, 7.6, 4.5 Hz). HRMS (EI+) exact mass calculated for $[M+\bullet]^+$ (C_8H_9FO) requires *m/z* 140.0637, found *m/z* 140.0636. $[\alpha]_D$ = -47.9 (c = 1.0, $CHCl_3$). Reported rotation for the *S*-enantiomer $[\alpha]_D$ = 52.5 (c = 1.1, $CHCl_3$).[8] Enantiopurity was determined by GLC using a Macherey-Nagel Hydrodex-B-TBDAc (50 m x 0.25 mm) column (110 °C isotherm); (*R*) isomer t_r = 57.1 min and (*S*) isomer t_r = 59.4 min.



(*R*)-2-Fluoro-3-phenyl-1-propanol (Table 2, entry 8): Prepared according to the general procedure from hydrocinnamaldehyde (263 μL, 2.00 mmol) to afford a colorless oil. Purification on silica gel (10-40% Et_2O/Pentanes) afforded (*R*)-2-fluoro-3-phenyl-1-propanol as a colorless liquid (218 mg, 71% yield, 96% ee), which matched literature data.[9] IR (film) 3369, 3029, 2932, 1497, 1455, 1052, 904.3, 835.6, 745.7, 700.0 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21-7.36 (m, 5H, $C_6\mathbf{H_5}$), δ 4.78 (dm, 1H, *J* = 48.6 Hz, FC**H**), δ 3.60-3.85 (m, 2H, OC$\mathbf{H_2}$), δ 2.87-3.10 (m, 2H, PhC$\mathbf{H_2}$), δ 1.97 (t, 1H, *J* = 6.1 Hz, -O**H**); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 136.3 (d, *J* = 6.0 Hz), 129.3, 128.6, 126.8, 95.6 (d, *J* = 170.6 Hz), 64.1 (d, *J* = 21.3 Hz), 37.4 (d, *J* = 20.0 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –187.6 (m). HRMS (EI+) exact mass calculated for $[M+\bullet]^+$ ($C_9H_{11}FO$) requires *m/z* 154.0794, found *m/z* 194.0797. $[\alpha]_D$ = 16.7 (c = 1.0, $CHCl_3$). Reported rotation for the *S*-enantiomer $[\alpha]_D$ = –17.6 (c = 1.7, $CHCl_3$).[8] Enantiopurity was determined by GLC using a Macherey-Nagel Hydrodex-B-TBDAc (50 m x 0.25 mm) column (120 °C isotherm); (*R*) isomer t_r = 76.1 min and (*S*) isomer t_r = 84.3 min.



(*R*)-2-Adamantyl-2-fluoro-1-ethanol (Table 2, entry 9): Prepared according to the general procedure from adamantylacetaldehyde (334 μL, 2.00 mmol) to afford a colorless oil. Purification on silica gel (5-20% EtOAc/Pentanes) afforded (*R*)-2-adamantyl-2-fluoro-1-ethanol as a colorless solid (326 mg, 82% yield, 98% ee). IR (film) 3306, 2903, 2850, 1451, 1348, 1087, 1058, 1028, 989.3, 859.0 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.07 (ddd, 1H, *J* = 49.7, 7.8, and 5.1 Hz, FC**H**), δ 3.62-3.88 (m, 2H, OC$\mathbf{H_2}$), δ 1.99 (s, 3H, C**H**$(CH_2)_3$) δ 1.54-1.84 (m, 13H, -O**H**, (C$\mathbf{H_2}$)$_6$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 101.8 (d, *J* = 170.3 Hz), 61.3 (d, *J* = 22.3 Hz), 37.7 (d, *J* = 4.1 Hz), 36.9, 35.4 (d, *J* = 19.6 Hz), 27.9 (*J* = 0.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ: –203.1 (ddd, *J* = 48.5, 34.2, 17.2 Hz). HRMS (EI+) exact mass calculated for $[M+\bullet]^+$ ($C_{12}H_{19}FO$) requires *m/z* 198.1420, found *m/z* 198.1417. $[\alpha]_D$ = –9.5 (c = 1.0, $CHCl_3$). Enantiopurity was determined by chiral HPLC analysis of the 2-naphthoyl derivative (Chiralcel®OJ Isocratic 3% *i*PrOH/Hexanes). t_R(major) = 20.8 min. t_R(minor) = 26.5 min.

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